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DIMERIZATION OF COBALT (II) TETRASULFONATED
PHTHALOCYANINE IN WATER AND A. (U) CHEMICAL RESEARCH
AND DEVELOPMENT CENTER ABERDEEN PROVING GRO.
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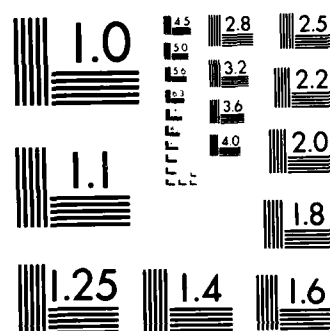
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**DIMERIZATION OF COBALT (II)
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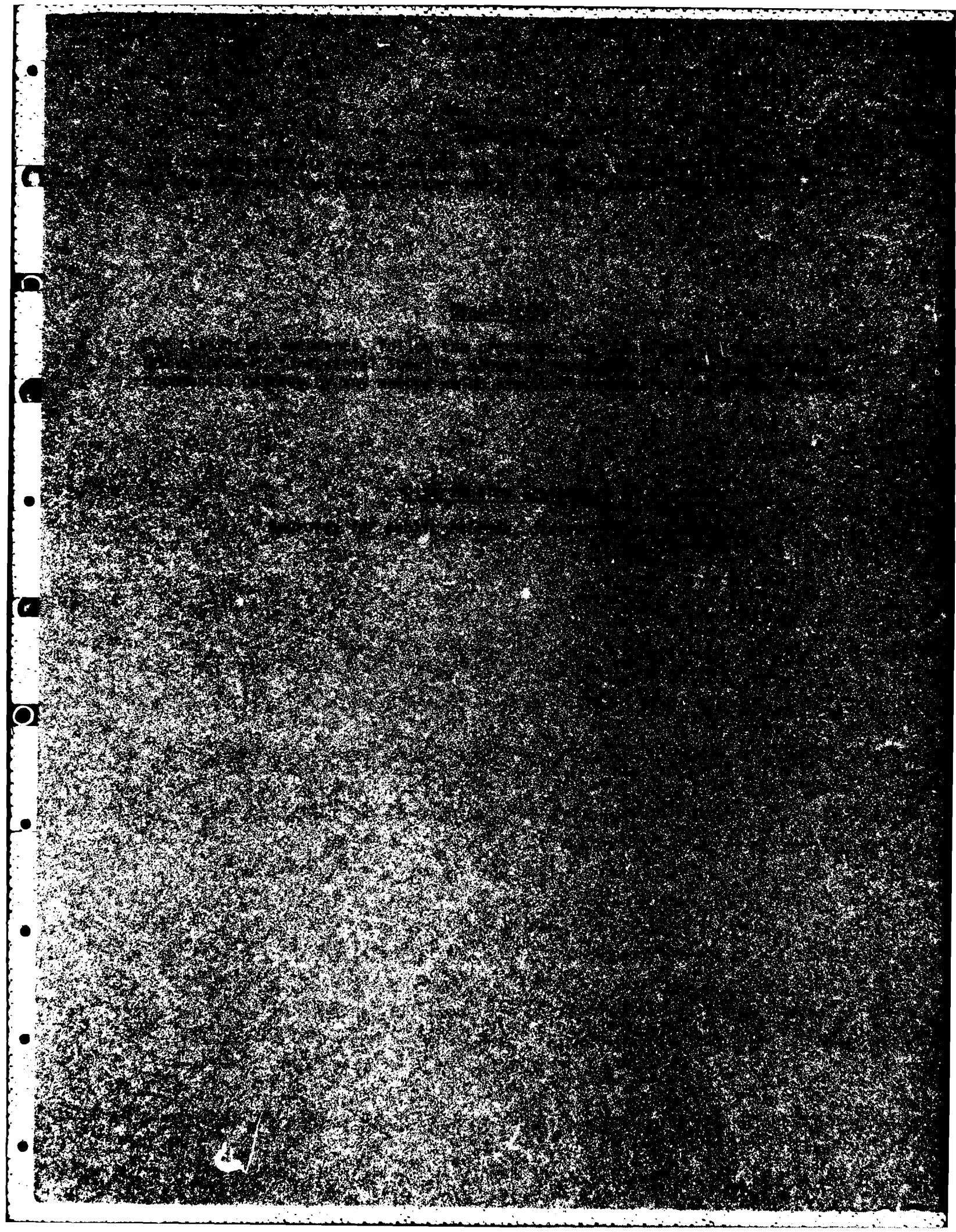
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<p>Metal complexes of tetrasulfonated phthalocyanine (TSPC) are of interest as oxidation and hydrolysis catalysts for thioethers and organophosphonates. Since metal TSPC complexes aggregate in aqueous solution, it was necessary to determine the dimerization constant as a prerequisite to establishing the efficacy of the monomeric Cobalt (II) TSPC (CoTSPC) complex as a catalyst. Since these potential catalysts will be used in mixed solvents to dissolve thioethers, the aggregation of CoTSPC was measured in alcohol-water solutions at various temperatures.</p> <p>This study uses a nonlinear, least-squares program to compute best-fit molar absorbances for monomers and dimers simultaneously. In addition, the monomer-dimer equilibrium is investigated over a wide temperature range, 5-75°C, in water to determine if the standard enthalpy of formation varies with temperature. It was found that the enthalpy was</p>				
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19. ABSTRACT (continued)

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↓
Temperature-dependent, possessing a constant value of ΔC_p of 0.1 kcal/mole-K. It was also shown that earlier investigators deduced dimerization constants that were smaller than the ones reported in this investigation. We feel this was caused by the presence of higher aggregates and unwarranted assumptions in the method to estimate the dimerization constant. It is also shown that the dye, CoTSPC, behaves as typical non-aqueous solute, and that hydrophobic bonding is not involved in the formation of the dimer. *Of course*

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PREFACE

This work was performed under Project 1L161101A71A, Research in Defense Sciences in FY83 and FY84 during the tenure of Dr. Yu-Chu Yang as a senior associate of the National Research Council.

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DIMERIZATION OF COBALT(II) TETRASULFONATED PHTHALOCYANINE IN WATER AND AQUEOUS-ALCOHOL SOLUTIONS

1. INTRODUCTION

Metal complexes of tetrasulfonated phthalocyanine (TSPC) (Figure 1), like other water-soluble dyestuffs, aggregate in aqueous solution.¹ The formation of the dimer has been the subject of repeated studies for a variety of transition-metal complexes with TSPC.²⁻¹⁰

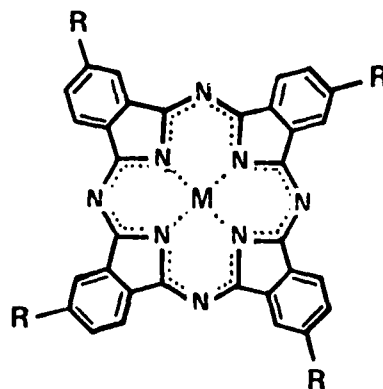


Figure 1. Structure of Metal Phthalocyanines

The equilibrium constant for forming a dimer in very dilute solutions can be obtained spectrophotometrically since TSPC complexes absorb strongly in the visible region. In the past, all methods employed to determine the dimerization constant of TSPC complexes spectrophotometrically required that the spectrum of the pure monomer be known. This spectrum is frequently obtained by successively diluting a dye solution until the spectrum does not change with temperature, or diluting the dye in alcoholic-aqueous solution to foster the presence of pure monomer in more concentrated solutions compared with the first method. In addition, in determining the monomer spectra, further approximations on the nature of the dimer spectrum are made, or the measured absorbance data are treated with mathematical approximations,^{4,8,11} so that the concentrations of the monomeric and dimeric species can be obtained to calculate the dimerization equilibrium constant.

This study uses a nonlinear least-squares program to compute the best-fit molar absorptivity for monomer and dimer simultaneously from absorbance measurements over a range of dye concentrations in which only monomer and dimer are present. It is illustrated with cobalt (II) TSPC (CoTSPC, $C_{32}H_{12}N_8O_{12}S_4Na_4Co \cdot 2 H_2O$, formula weight = 1016 gm) as the dyestuff, and results are compared with published work. In addition, the monomer dimer equilibrium of Cobalt (II) TSPC (CoTSPC) is investigated for temperatures ranging from 5 to 75°C in water to determine if the standard enthalpy of formation, ΔH° , is a function of temperature. The equilibrium is also investigated in aqueous alcohol solvent systems including methanol, ethanol and isopropanol between 25 and 45°C.

2. EXPERIMENTAL

2.1 Preparation of [29H,31H-phthalocyanine-2,9,16,23-tetrasulfonato(2)-N²⁹, N³⁰, N³¹, N³²] Cobalt (CoTSPC).

This material was prepared using the method of Weber and Busch¹² who used the sodium salt of 4-sulfophthalic acid, ammonium chloride, urea, ammonium molybdate, and cobalt sulfate heptahydrate in hot nitrobenzene. The purification procedure for this 0.05-mole scale reaction differed slightly from the published method. The crude, dark-blue product was broken apart with a spatula, rinsed with 400 ml methanol, and finely ground in a mortar. The resulting blue powder was dissolved in 1.1 liter of 1N HCl saturated with sodium chloride to give a deep blue slurry that was heated to reflux briefly, then cooled to room temperature and filtered. The air-dried product was dissolved in 700 ml of 0.1N sodium hydroxide, heated to 80°C and filtered (no residue). Sodium chloride (270 gm) was added to salt out the product. This slurry was heated with stirring at 80°C for 3 hours while ammonia evolved. Upon cooling to room temperature, the product was isolated by filtration. This reprecipitation was repeated twice and the final precipitate was washed with 1.8 liters of 80 percent aqueous ethanol to remove occluded sodium chloride (NaCl). A convenient final purification was achieved by washing the blue powder in the thimble of a Soxhlet apparatus with hot 95 percent ethanol for 18 hours. The product was then dried in vacuo for 2 days to yield 22 gm (54 percent) of the desired CoTSPC as determined by UV-visible (UV-VIS) spectroscopy.

2.2 Spectrophotometric Measurements.

All spectrophotometric measurements are made with a diode array UV-VIS spectrophotometer (HP 8450A) equipped with a temperature controller (HP 89100A). The equipment is controlled by a microcomputer to provide at least six repeated

measurements of each sample at 1-minute intervals starting about 5 minutes after the cell compartment reaches the controlled temperature.

All of the sample solutions were freshly made on the same day when absorbances were measured to avoid errors caused by evaporation of the solvents and absorption of the dye to the walls of the glass containers (Appendix A).

2.3 Methods for Determining Molar Absorbances.

The absorbance of a solution in a 1-cm cell containing only monomer and dimer is

$$A = \epsilon_M [M] + \epsilon_D [D] \quad (1)$$

where A = absorbance

ϵ_M = molar absorption coefficient, monomer, $M^{-1}cm^{-1}$

ϵ_D = molar absorption coefficient, dimer, $M^{-1}cm^{-1}$

$[M]$ = monomer concentration, M

$[D]$ = dimer concentration, M .

Note that ϵ_D and $[D]$ are on the basis of the dimer molecular weight of 2,032 gm/mole, twice that of the monomer specie. The equilibrium between monomer and dimer is

$$K_D = \frac{[D]}{[M]^2} \quad (2)$$

where K_D = dimerization constant, M^{-1} , assuming that the activity coefficients of the dye species are close to unity. The total concentration of CoTSPC, C_T , is

$$[C_T] = [M] + 2[D] \quad (3)$$

Equations (2) and (3) can be combined to give the monomer concentration in terms of total CoTSPC as

$$[M] = \frac{-1 + \sqrt{1 + 8K_D [C_T]}}{4K_D} \quad (4)$$

With Equations (2)-(4), one can rewrite Equation (1) in terms of the experimentally accessible total concentration of CoTSPC as

$$A = \epsilon_M \left(\frac{-1 + \sqrt{1 + 8K_D(C_T)}}{4K_D} \right) + \frac{\epsilon_D}{2} \left[(C_T) - \left(\frac{-1 + \sqrt{1 + 8K_D(C_T)}}{4K_D} \right) \right] \quad (5)$$

The absorbances of 18 solutions of different CoTSPC concentrations were measured at the peak absorbance of 662nm after temperature equilibration. A non-linear, least-squares program¹³ based on the Gauss-Newton technique was used to fit the measured absorbances versus $[C_T]$ in equation (5). Following a procedure recommended by Monahan,¹⁴ the value of ϵ_M was fixed and those for ϵ_D and K were allowed to vary. Best-fit values of ϵ_D were obtained at each of several temperatures; these values were averaged to get a mean value of ϵ_D . Values of K were then computed from Equation (5) with the values of ϵ_M and ϵ_D fixed. Runs were also made with all three parameters varying in order to compare the best-fit ϵ_M with the value of ϵ_M obtained independently in alcohol-water mixtures.

3. RESULTS

3.1 CoTSPC Spectrum in Water.

Figure 2 illustrates the spectra of a $2 \times 10^{-5}M$ solution of CoTSPC in water at temperatures ranging from 20 to 85°C at 10-degree intervals. An isosbestic point appears at 634nm. Aggregates larger than the dimer are presumed to be absent.²⁻⁸

The measured absorbances were corrected for the changes in volume of the solutions at higher temperatures; these correction factors are listed in Appendix B along with other pertinent physical properties.

3.2 Measured Spectrum of Pure Monomer.

The molar absorptivity for the pure monomer species was measured by each of the two methods described previously. Table 1 lists the absorbances at λ_{max} (662nm) for a series of solutions as a function of temperature. This method is limited to the precision obtainable in dilute solutions. Replicate measurements revealed that the absorbances could be measured with a standard deviation of 5×10^{-4} absorbance unit. Since the observed absorptivity still appears to be increasing as concentration is lowered, even at 75°C, one can only conclude that ϵ_M is between 1.1 to $1.2 \times 10^5 M^{-1}cm^{-1}$. In addition, the

Table 11. CoTSPC Dimerization Constant in Water at 58°C^a

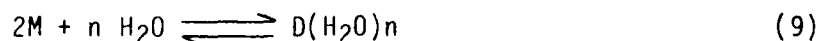
$C_T \times 10^6 M$	$C_M \times 10^6 M$	$K_D, M^{-1} \times 10^{-5}$
0	-	2.05 ^b
1.0	0.85	1.11
2.2	1.9	0.62
4.9	3.6	0.50
7.2	5.0	0.44
9.8	6.4	0.42

^aThe numbers were estimated from Figure 3 in Reference 8.

^bReported value of K in Reference 8.

To test this further, conductivity measurements were made of dilute CoTSPC solution (Table 12) which also show that little or no change in conductivity is observed in the concentration region in which Eyring and co-workers saw the dramatic change in K.

Abel and co-workers² also determined the dimerization of CoTSPC in a series of methanol-water and ethanol-water solutions at 20°C. They found that a plot of $\log K_D$ versus $\log [H_2O]$ was linear and that the slope was the same for ethanol or methanol aqueous solutions. They concluded that the dimerization of CoTSPC involved incorporation of water according to



Our results contradict this interpretation since we find that the dimerization constant decreases for a given mole fraction of alcohol as one goes from methanol to ethanol. Our results on the effect of alcohol-water on dimerization are more in line with Dewey and co-workers¹⁷ who found that the dimerization constant of thionine decreased markedly as ethanol content increased, and that the dimerization constant was smaller for a given mole fraction of alcohol in ethanol than in methanol (Table 13). Figure 4 illustrates K_D versus mole percent ethanol at 25°C for CoTSPC where one sees that dimerization is almost absent at 0.10 X_2 . It is unclear whether the value of K_D at 2.5 mole percent EtOH (0.025 X_2)

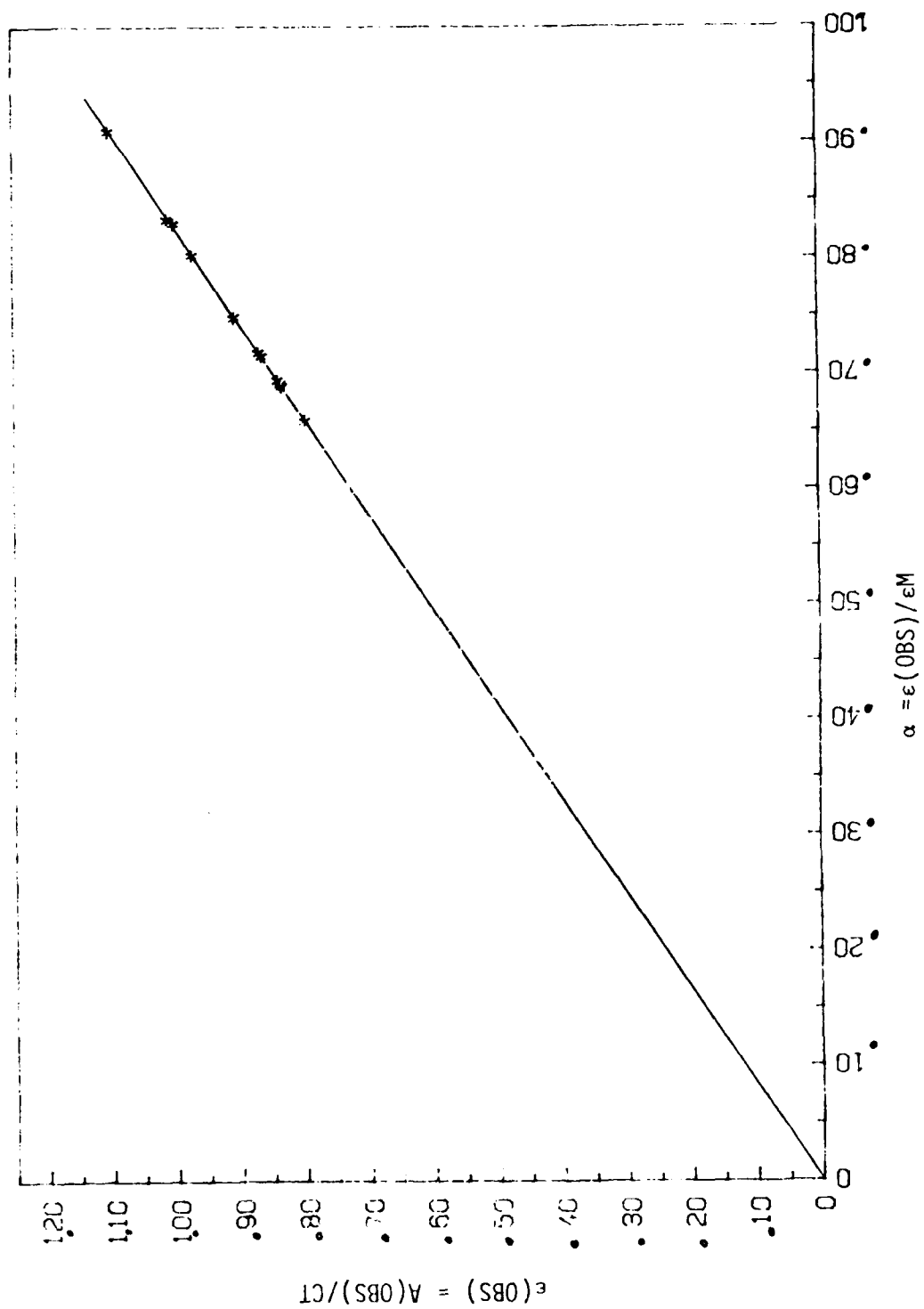


Figure 3. $\epsilon(\text{OBS})$ versus α at 75°C

So one is actually plotting ϵ versus ϵ/ϵ_M . Obviously, the method also depends on the chosen value of ϵ_M which accounts, in part, for the discrepancy between Abel² and Gruen.¹⁰ We tried to use this method with our data using values >0.8 ; we obtained a value of ϵ_D near zero (Figure 3).

4.3 Dimerization Constant of CoTSPC.

The above approximation that α equals ϵ/ϵ_M has also been used frequently to obtain the dimerization constants,^{4,16} since

$$K = \frac{(1-\alpha)}{2\alpha^2} [C_T] \quad (8)$$

One need only know ϵ , ϵ_M , and $[C_T]$ to obtain a value of K . One of the characteristics of dimerization constants obtained in this fashion is that K varies with $[C_T]$ which Sheppard¹⁶ attributed to activity effects. One also notes that plots of $\log [M]$ versus $\log [D]$ had slopes of 1.8-1.9 rather than 2 as required by the law of mass action. Such differences were deemed insignificant. However, these differences result in values of K about 12 percent smaller than would have been obtained if the slope were 2 for $[C_T] = 1 \times 10^{-6}M$. We feel the problem is that the quantity $(\epsilon_D/2)(1-\alpha)$ cannot be ignored, especially since we have shown, at least for CoTSPC, that ϵ_D is larger than expected on the basis of the extrapolation to zero α . In such cases, neglecting the second part of Equation (7) results in values which are too small, and result in underestimated values of K . As the total concentration of dye increases, the error in α is worse, and K decreases with increasing $[C_T]$.

Eyring and co-workers^{7,8} also noted this trend of K decreasing as $[C_T]$ increases, and the values of K in Table 7 represent extrapolations to $[C_T] = 0$. Table 11 shows some of Eyring and his co-workers' results in more detail. To explain their results, Eyring and co-workers^{7,8} also invoked the argument concerning activity effects. For dimerization of a charged molecule, one would expect that the increase in ionic strength should increase dimerization. This is confirmed by experiments with salt added;¹⁷ Table 8 shows Abel and co-workers' results² for salt added to methanol-water solutions of CoTSPC in which the apparent K increases.

Table 10. Monomer Concentration by Successive Approximation Method for Dye (II) (p-toluenesulfonate) in Water at 553nm^a

$C_T \times 10^5 M$	Aobs/cell length (cm)	$M \times 10^5 M$	$D \times 10^5 M$	$\epsilon_D' M^{-1} cm^{-1} \times 10^{-5}^b$
1.00	1.19/1	0.70	0.15	0.40
1.93	1.01/0.5	1.14	0.40	0.45
2.00	1.04/0.5	1.16	0.42	0.48
2.88	0.28/0.1	1.48	0.70	0.57
3.00	0.58/0.2	1.60	0.70	0.43
4.00	0.71/0.2	1.94	1.03	0.39
5.00	0.86/0.2	2.28	1.36	0.44
10.00	0.32/0.05	3.28	3.36	0.30
20.00	0.51/0.05	9.66	7.67	0.34

^aAll data except ϵ_D' were obtained from Table 2 of Reference 11.

^bCalculated for 1-cm cell, $\epsilon_D' = 1/2 \epsilon_D$. ϵ_D' was also reported to be 0.32×10^5 by extrapolating observed ϵ to $\alpha = 0$ at 553nm in Reference 11.

Table 8. Dimerization Constant of CoTSPC in 20 percent MeOH at 20°C^a

$C_T \times 10^5 \text{ M}$	$\epsilon_D, \text{M}^{-1}\text{cm}^{-1} \times 10^{-5}^b$	$K_D, \text{M}^{-1} \times 10^{-5}^c$	Added KClO_4
1.94	NA	0.31	0
2.0	0.67	2.2	$5 \times 10^{-3}\text{M}$
1.0	0.67	2.6	$5 \times 10^{-3}\text{M}$
0.5	0.64	3.0	$5 \times 10^{-3}\text{M}$
0.25	0.55 ^d	2.7 ^d	$5 \times 10^{-3}\text{M}$

^aFrom Reference 2^b ϵ_D' was calculated from the reported data on absorbances at 662nm, monomer concentrations, and $\epsilon_M = 1.04\text{E}5$.^cTaken from data in Reference 2^dIf ϵ_D' remains $0.67 \times 10^5 \text{M}^{-1}\text{cm}^{-1}$; then K is calculated to be $3.6 \times 10^5 \text{M}^{-1}$. This shows that K increases steadily as $[C_T]$ decreases in the presence of the KClO_4 .

Table 9. Absorbances of CoTSPC in Pure Methanol and Methanol-Water Mixtures at 20°C

$[C_T], \text{M} \times 10^6$	Solvent	$\lambda_{\text{Max}}, \text{nm}$	$\epsilon_{\text{max}}, \text{M}^{-1}\text{cm}^{-1} \times 10^{-5}$	$\epsilon_{662}, \text{M}^{-1}\text{cm}^{-1} \times 10^{-5}$
0.74	MeOH	658	1.21	1.10
4.36	MeOH	658	1.21	1.10
7.40	MeOH	656	1.22	1.09
6.89	20% MeOH ^a	662	1.06	1.06
6.30	30% MeOH ^b	662	1.06	1.06
7.40	50% MeOH ^c	662	1.07	1.07

^aMole fraction of MeOH = 0.10^bMole fraction of MeOH = 0.15^cMole fraction of MeOH = 0.30

Table 7. Summary of Published Data on CoTSPC Dimerization in Water

Temp °C	λ_{max} , nm	ϵ_M , $M^{-1}cm^{-1}$ $\times 10^{-5}$	ϵ_D , $M^{-1}cm^{-1}$ $\times 10^{-5}^a$	K_D , M^{-1} $\times 10^{-5}^b$	Reference
20	662 664	1.04 ^c 1.21	0.33 ^d	4.03×10^5 ^e	2
NA	663	1.21 ^f	0.48 ^d	NA	10
58	663	1.03 ^g	NA	2.05×10^5	7
48	663	1.03	NA	4.7×10^5	7
38	663	1.03	NA	8.0×10^5	7
NA	663	1.25 ^h	NA	NA	15

^a $\epsilon_D' = 1/2\epsilon_D$

^bDetermined by the method described in Reference 11

^c1.04 determined from 60% MeOH, 1.21 determined from 50% EtOH

^dEstimated from Figure 2 in Reference 10 for calculated dimer spectrum

^e $\epsilon_M = 1.04 \times 10^5$ was used for calculating K

^fDetermined from 20% EtOH

^gDetermined from a $10^{-7}M$ dye in water at 81°C

^hDetermined from EtOH-H₂O solutions

4. DISCUSSION

The published values of ϵ_M , ϵ_D , and K for CoTSPC are listed in Table 7 while data for dimerization in methanol-water solutions are contained in Table 8. In the following sections, these values will be compared separately with our results.

4.1 Monomer Molar Absorptivity

As discussed earlier, $\epsilon_M = 1.21 \times 10^5 \text{M}^{-1}\text{cm}^{-1}$ is consistent with earlier determinations in alcohol-water solutions. Interestingly, previously reported values of K used a value of $1.03 \times 10^5 \text{M}^{-1}\text{cm}^{-1}$ which is significantly smaller than $1.21 \times 10^5 \text{M}^{-1}\text{cm}^{-1}$. Eyring, and coworkers^{7,8} determined ϵ_M by heating CoTSPC solution in water; however, we found that when this method was used, it was difficult to obtain a precise value for ϵ_M . In methanol-water, shifts in the maximum peak of the monomer was observed (Table 9). It is interesting to note that the same value of ϵ_M was found at 658nm in pure methanol that was found in the other solvents with peak absorbance at 662nm.

4.2 Dimer Molar Absorptivity.

Few values of ϵ_D have been reported for CoTSPC since measurements of the dimerization constant were made with West and Pearce's method.¹¹ Their method only requires a knowledge of ϵ_M after which assumptions can be made of the dimer spectrum. We used results from West and Pearce,¹¹ and tried to recalculate ϵ_D for a dye that they used to illustrate their technique. Our results are shown in Table 10. We see that ϵ_D varies considerably as $[C_T]$ varies.

The ϵ_D values^{2,10} listed in Table 8 were obtained from a plot of absorptivity versus α defined as the fraction of CoTSPC present as monomer. The value of ϵ at $\alpha = 0$ is taken as ϵ_D . The value of α is determined in the following manner. By definition

$$\epsilon = \epsilon_M \alpha + \frac{\epsilon_D}{2} (1-\alpha) \quad (6)$$

It is assumed that the second term can be neglected and

$$\alpha = \epsilon / \epsilon_M \quad (7)$$

Table 6. Dimerization Constants of CoTSPC in Alcohol-Water Solutions

Solvent	x_2	$K_D, M^{-1} \times 10^{-5}^a$		
		25°C	35°C	45°C
Water	-	84.0	41.0	23.0
MeOH	0.10	1.4	0.88	0.52
	0.15	0.63	0.52	0.38
EtOH	0.025	84.0 ^b	15.0	8.2
	0.050	22.0	10.0	6.9
	0.080	8.1 \pm 1.3	5.0 \pm 1.1	3.5 \pm 0.9
	0.10	1.0	0.79	0.60
	0.15	0.19 \pm 0.08	0.16 \pm 0.01	0.16 \pm 0.02
iPrOH	0.15	0.22		

^aError represents sample standard deviation where noted. Other values are single determinations.

^bTotal CoTSPC concentration was $4.10 \times 10^{-6} M$, so it is possible that higher aggregates may be present.

Table 5. Dimerization Constants Calculated with ϵ_M and ϵ_D Fixed*

[C _T], M x 10 ⁷ Temp (°C)	K _D , M ⁻¹ x 10 ⁻⁶					
	25	35	45	55	65	75
0.879	7.4	3.5	2.6	1.5	0.89	0.64
1.88	7.9	3.9	2.5	1.4	0.92	0.61
1.95	8.2	3.8	2.5	1.4	0.88	0.63
2.27	8.2	3.9	2.4	1.4	0.88	0.64
2.52	8.4	4.0	2.3	1.4	0.89	0.63
2.36	8.8	4.4	2.3	1.4	0.88	0.64
4.40	8.9	4.6	2.1	1.4	0.89	0.63
5.23	9.3	5.0	2.1	1.4	0.88	0.65
9.11			1.9	1.3	0.85	0.65
11.4				1.4	0.83	0.64
20.9				1.3	0.80	0.69
52.3						0.74
Mean	8.4	4.1	2.3	1.4	0.87	0.64
Std dev	0.6	0.5	0.2	0.1	0.03	0.02

$$*\epsilon_M = 1.21 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$$

$$\epsilon_D = 1.60 \times 10^5 \times \text{M}^{-1} \text{ cm}^{-1}$$

temperatures. This result is also consistent with the assumption that higher aggregates are present despite the isosbestic point evident in Figure 2. From Table 4 the mean value of ϵ_D is $(1.60 \pm 0.08) \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$. Values of K were then computed with ϵ_M and ϵ_D fixed as shown in Table 5.

Table 4. Calculated ϵ_D and K at $\epsilon_M = 1.21 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ for Various Concentration Ranges

Temp (°C)	Conc (M)	$\epsilon_D \times 10^{-5}$
25	9×10^{-8} to 5×10^{-7}	$1.54 \pm 0.14^*$
35	9×10^{-8} to 1×10^{-6}	1.46 ± 0.15
45	9×10^{-8} to 1×10^{-6}	1.70 ± 0.11
55	9×10^{-8} to 2×10^{-6}	1.63 ± 0.05
65	9×10^{-8} to 2×10^{-6}	1.65 ± 0.04
75	9×10^{-8} to 5×10^{-6}	1.57 ± 0.02

*Standard deviation from non-linear, least-squares program.

3.4 Dimerization of CoTSPC in Alcohol-Water Mixtures.

Dimerization constants were measured in methanol, ethanol, and isopropanol water mixtures. Results of individual absorbance measurements are listed in Appendix D. For a few mixtures, values of ϵ_D in ethanol-water were determined with ϵ_D varying and ϵ_M fixed as was done with values in water. The value of ϵ_D was close to the value from water ($1.5 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$). Again one concludes that the molar absorptivities are unaffected by co-solvent and that only monomer-dimer equilibria is significant. Then values of K were calculated with ϵ_M and ϵ_D fixed. For other alcohol-water solutions, only one solution was made for a given mixture. The values of K are summarized in Table 6 where one sees that for a given mole fraction of alcohol, dimerization constants are larger in methanol than in ethanol, and K_D decreases as alcohol is added to water. Because the volume changes are so large in the alcohol-water solutions, only data to 45°C is considered.

TABLE 2. Absorptivity of CoTSPC at 662nm in Ethanol-Water Solutions at 35°C

20% EtOH ^a		40% EtOH		60% EtOH	
$[C_T]^b$	ϵ_a^c	$[C_T]^b$	ϵ_a^c	$[C_T]^a$	ϵ_a^c
0.202	1.14	0.204	1.22	0.201	1.21
1.01	1.11	1.02	1.19	1.01	1.23
2.02	1.07	2.04	1.18	2.01	1.24
10.1	1.07	10.2	1.14	10.1	1.22
		20.4	1.08	20.1	1.08

^aPercent by volume^b $M \times 10^6$ ^c $M^{-1}cm^{-1} \times 10^{-5}$ TABLE 3. Fitted Values of ϵ_M and ϵ_D Using Equation (5)

Temp (°C)	$\epsilon_M, M^{-1}cm^{-1} \times 10^{-5}$	Std dev	$\epsilon_D, M^{-1}cm^{-1} \times 10^{-5}$	Std dev
5	1.03	0.20	0.67	0.04
15	1.10	0.39	0.67	0.08
25	1.19	0.36	0.72	0.07
35	1.17	0.23	0.76	0.08
45	1.12	0.08	0.80	0.06
55	1.13	0.07	0.92	0.06
65	1.17	0.08	1.18	0.05
75	1.18	0.09	1.32	0.05

observed value of ϵ did not vary much between $1.88 \times 10^{-7}M$ and $5.23 \times 10^{-7}M$; therefore, it is also difficult to extrapolate $[C_T]$ to zero as suggested in Reference 11.

The second method used measured ϵ_M in alcohol-water solutions. The maximum absorption of monomer in pure ethanol occurs at the same wavelength in water (662nm), but the peak shifts to 658nm in pure methanol. Since the solubility of CoTSPC in pure ethanol was too small to measure accurately, attention shifted to ethanol-water solutions. By contrast, the solubility in methanol was sufficient to show that Beer's Law holds and that CoTSPC exists as the monomer in pure methanol. The absorptivities of three ethanol-water mixtures at 35°C are listed in Table 2. Beer's Law applies in 60 percent ethanol (EtOH) to $1 \times 10^{-5}M$ CoTSPC and to $2 \times 10^{-6}M$ CoTSPC in 40 percent EtOH from which a value of $\epsilon_M (1.21 \pm 0.02) \times 10^5 M^{-1}cm^{-1}$ is computed. Presumably, dimer is present in the other ethanol-water solutions. Sorek and co-workers¹⁵ also reported a value of $1.2 \times 10^5 M^{-1}cm^{-1}$ for ϵ_M in alcohol-water solutions.

3.3 Determination of ϵ_D and K.

Eighteen solutions ranging from 8×10^{-8} to $2 \times 10^{-5}M$ CoTSPC were used to determine ϵ_D and K. The absorbances of these solutions were measured at $\lambda = 662nm$ from 5-75°C at 10°C intervals and then fit to Equation (5) with the nonlinear, least-squares program. In order to compare the best-fit ϵ_M in water with that measured in alcohol-water, the first calculations were done with ϵ_M , ϵ_D , and K allowed to vary. Results are listed in Appendix C. Table 3 summarizes the ϵ_M and ϵ_D values. One notes that the standard deviation progressively decreased as temperature increased while the values of ϵ_D steadily increased with temperature. This suggests that aggregates higher than the dimer may be present at the lower concentration. Nonetheless, one notes that the values of ϵ_M at 65 and 75°C agree well with the value of $1.21 \times 10^5 M^{-1}cm^{-1}$ measured in alcohol-water and in water. Thus, the addition of co-solvent does not alter the spectrum of CoTSPC monomer, an implicit assumption in most work with dye aggregates.

Calculations continued to determine ϵ_D with a method proposed by Monahan¹⁴ in which ϵ_M is fixed and ϵ_D and K are allowed to vary. However, computations were redone with higher concentrations progressively removed. These results are summarized in Table 4 where one sees that ϵ_D approached a common value at 25°C and higher as the higher concentrations were removed at the lower

Table 1. Absorbances Measured at $\lambda = 662\text{nm}$ in Pure Water

$[C_T], M \times 10^7$	45°C^a	55°C^a	65°C^b	75°C^b	$\epsilon_M, 75^\circ\text{C}, M^{-1}\text{cm}^{-1} \times 10^{-5}$
0.879	0.0101	0.0101	0.0102	0.0102	1.16
1.88	0.0202	0.0202	0.0214	0.0204	1.09
1.95	0.0202	0.0212	0.0214	0.0214	1.10
2.27	0.0222	0.0242	0.0245	0.0245	1.08
2.52	0.0253	0.0253	0.0265	0.0275	1.09
3.36	0.0343	0.0354	0.0367	0.0367	1.09
4.40	0.0448	0.0455	0.0469	0.0469	1.07
5.23	0.0535	0.0545	0.0561	0.0551	1.05
9.11	0.0879	0.0919	0.0938	0.0949	1.04
-	-	0.111	0.115	0.117	1.03

^aVolume correction of 1.01^bVolume correction of 1.02

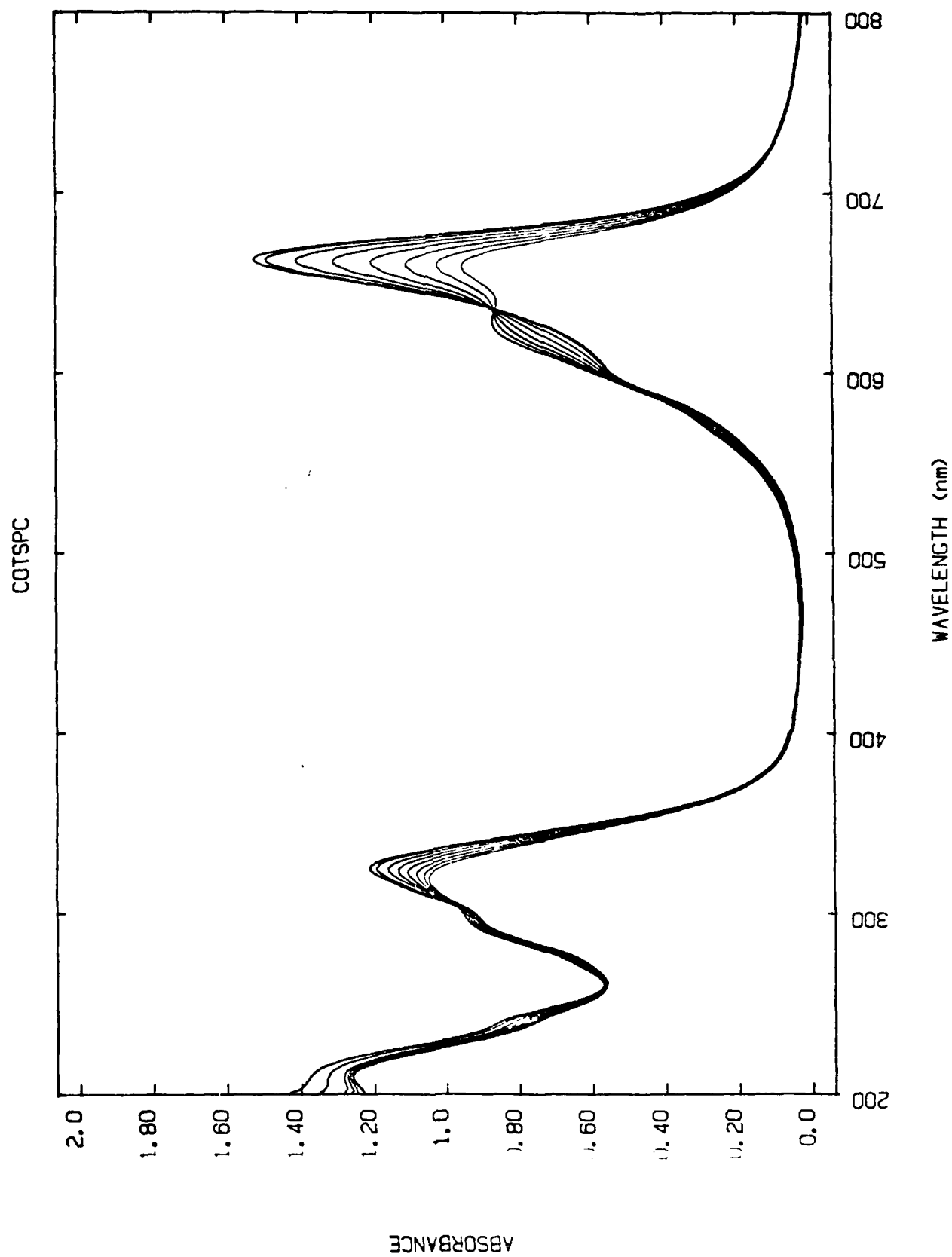


Figure 2. Spectrum of COTSPC Solution in Pure Water at Various Temperatures

Table 12. Conductivities of CoTSPC Solutions in Water at 25°C

$C_T, M \times 10^7$	$\kappa, \mu S/cm^a$	$Z, \mu S/cm^b$
1.42	0.00	0.0284
7.10	0.00	0.142
28.4	0.23	0.568
71.0	0.52	1.42
142.0	0.49	2.84
675.0	2.84	13.5

^aObtained by subtracting the measured conductivities from the conductivity of deionized water, $\kappa = 2.15 \mu S/cm$, used for solution preparation; $\mu S/cm = \omega^{-1}cm^{-1} \times 10^{-6}$.

^b Z is calculated conductivity of pure Na^+ ion at four times the same concentrations of the dye at 25°C. Since κ is lower than Z , ion-pairing may be present at the four terminal sodium sulfonate groups of CoTSPC.

Table 13. Effect of Solvent on Thionine Dimerization at 22°C^a

Solvent ^a	K, M^{-1}
Water	2,660
1% EtOH	635
5% EtOH	140
10% EtOH	35
10% MeOH	1125
1% PrOH	360
10% PrOH	C

^aReference 17

^bMole percent alcohol

^cToo small to measure

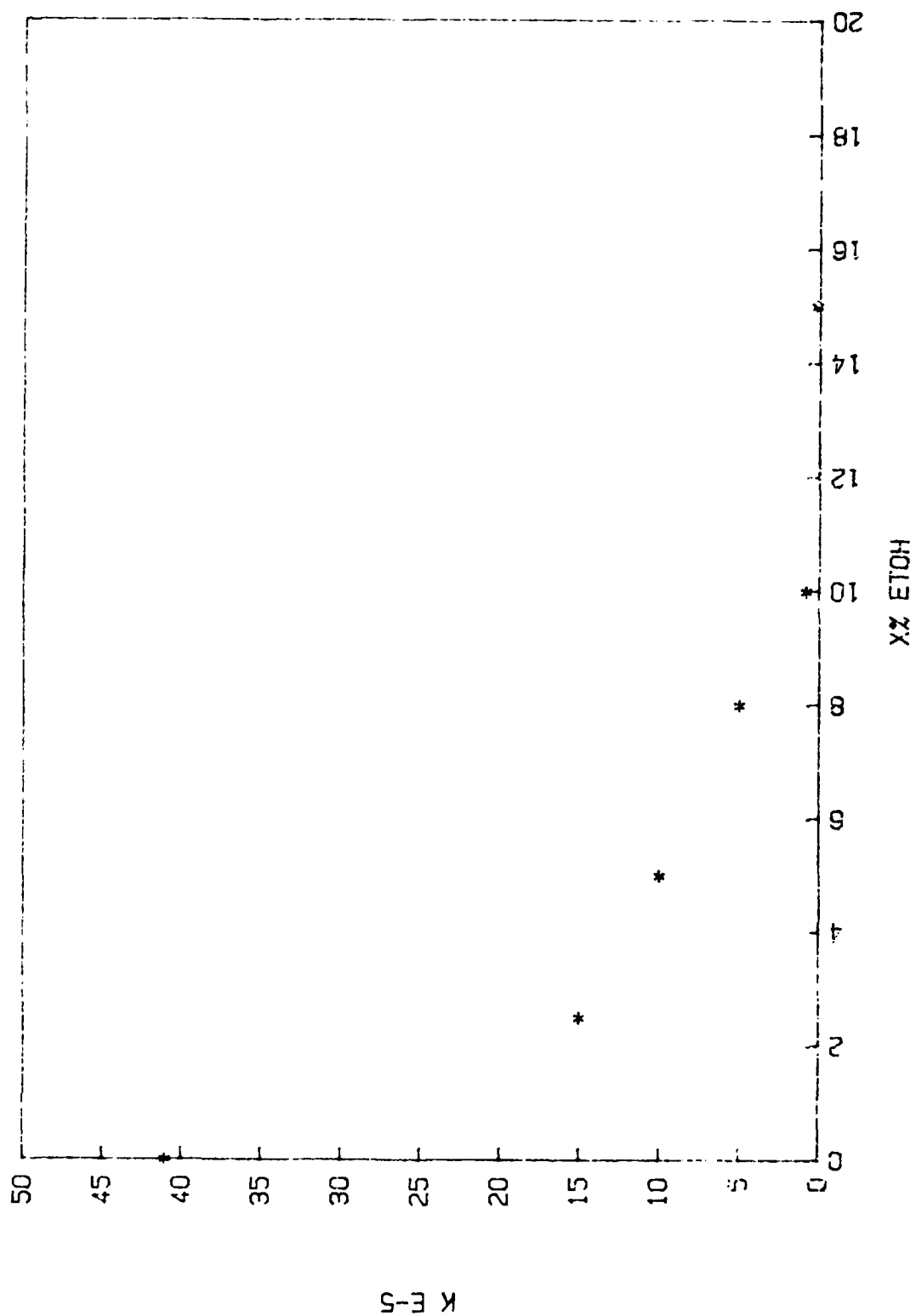


Figure 4. Dimerization of CoTSPC in EtOH-Water Solutions at 35°C

should be smaller to conform with the trend seen with the other points. Future experiments need be done in which replicate measurements at various mole fractions are collected.

4.4 Thermodynamics of CoTSPC Dimerization in Water.

Another facet of this study was to see if a finite heat capacity could be detected for the dimerization of CoTSPC. Since World War II, many examples of temperature-dependent activation energies have been measured¹⁸ along with more rigorous methods to test rate or equilibrium constants for non-zero heat capacities.¹⁹ We elected to use a method proposed by Blandamer, Robertson, and co-workers²⁰ which is discussed in more detail in Appendix E. Table 14 lists the values of enthalpy (ΔH) and ΔC_p computed with Blandamer and co-workers' method which suggests a constant, positive value of ΔC_p for dimerization. To confirm this, the values of ΔH in Table 14 were fit to

$$\Delta H = a + bT \quad (10)$$

where T is in $^{\circ}\text{C}$. The result gave values of a and b of -16.20 ± 0.32 kcal/mole and 113 ± 6 cal/mole-K for a and b , respectively, indicating that the dimerization of CoTSPC has a positive, constant value of ΔC_p . Table 15 lists the free energy, enthalpy, and entropy as a function of the temperatures studied.

A number of factors have been proposed to account for forces contributing to dimerization of dye molecules such as van der Waals forces, charge-charge interactions, hydrophobic interactions, or the role of the water.¹ The presence of a positive heat capacity of activation rules out hydrophobic interaction as a major contributor since hydrophobic interactions display a negative heat capacity as recently discussed by Evans and Lumry.²¹ Evans and Lumry point out that since the unique structure of water imposes contributions to ΔH and entropy (ΔS) that compensate and do not alter the free energy, it is dangerous to use their values near room temperature. This compensation between ΔH and ΔS for CoTSPC dimerization is aptly demonstrated in Figure 5. Evans suggests that one use hydrazine in place of water since it is identical to water except for the "ice-structure." To illustrate this and show the extent of the ΔH terms, Evans compared the thermodynamics of transfer of argon from hydrazine to water. This free energy transfer is only 0.4 kcal/mole at 25°C , but ΔH is -5/cal/mole, and ΔS is -15.4 cal/mole-K. Another way to avoid the confusion from this compensatory contribution to ΔH and ΔS is to examine data at high temperatures

Table 14. Calculation of ΔH and ΔC_p for CoTSPC Dimerization in Water with Blandamer's Method*

Temp, °C	ΔH , kcal/mole	ΔC_p , cal/mole-K
25	-13.34 \pm 0.14	112 \pm 8
35	-12.19 \pm 0.18	111 \pm 13
45	-11.08 \pm 0.68	110 \pm 9
55	- 9.94 \pm 0.14	107 \pm 14
65	- 0.25 \pm 0.29	98 \pm 19
75	- 7.41 \pm 0.16	122 \pm 8

*Errors are the standard deviation of the mean as computed by the program.

Table 15. Thermodynamics of CoTSPC Dimerization in Water

Temp, °C	ΔC° , kcal/mole	ΔH° , kcal/mole	ΔS° , cal/mole-K
25	-9.4	-13.4	-13.4
35	-9.3	-12.2	- 9.4
45	-9.2	-11.1	- 5.9
55	-9.2	-10.0	- 2.4
65	-9.2	- 8.8	1.1
75	-9.3	- 7.7	4.5

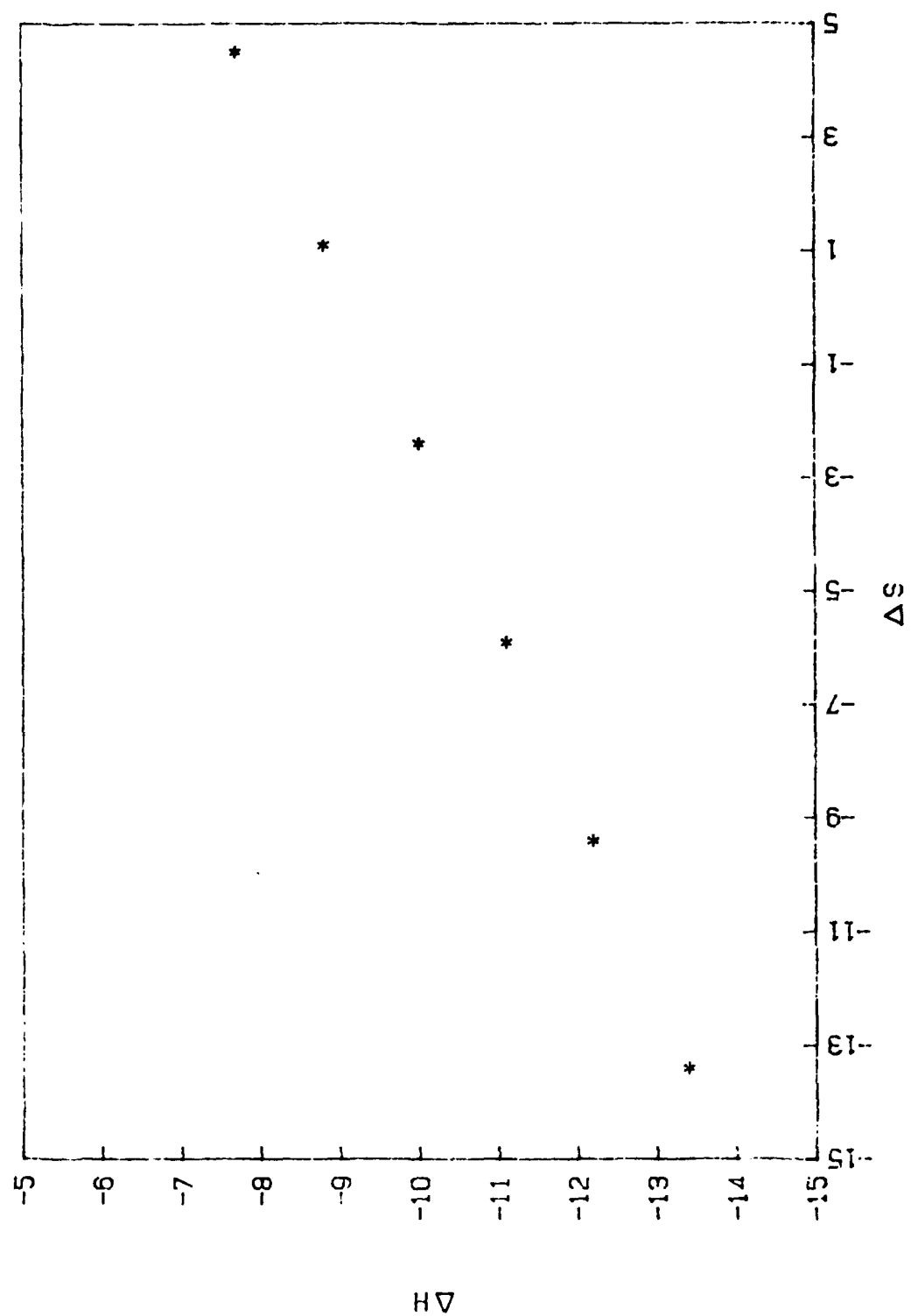


Figure 5. Enthalpy versus Entropy of Dimerization

where the unique water structure disappears. Using values of ΔH and ΔS at 75°C, one sees that the dimerization process has a positive entropy. Because the formation of a dimer should produce a negative entropy, a sizeable contribution to entropy may come from the release of water molecules on dimer formation. This is further substantiated by a recent article by Ohling^{21,22} who measured the pressure dependence of dimerization of methylene blue and pyronine G dyes. He found that the volume change on dimerization was negative and attributed it to the release of water on dimer formation. Thus, we agree with Abel and co-workers² that water participates in dimer formation; however, we find that water is released into the bulk solvent when the dimer forms as opposed to their contention that water is incorporated into the dimer.

Another piece of evidence to support our contention that hydrophobic bonding does not contribute to dimerization is the rapid dissolution of CoTSPC in water as opposed to alcohol which is characteristic of an electrolyte as opposed to a hydrophobic solute.

Finally, enthalpies and entropies of dimerization in alcohol-water solutions were not calculated to collect replicate runs at various mole fractions to improve the precision of the dimerization constants in these solvents.

5. CONCLUSIONS

As a result of the study conducted, the following conclusions are provided:

- Published results on ϵ_M and ϵ_D of CoTSPC in aqueous solutions were inconsistent. The values determined from this work, $\epsilon_M = 1.21 \times 10^5$ and $\epsilon_D = 1.60 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$, are higher than the published values.
- Published results on the dimerization constants were too low because the successive approximation method for monomer concentration tends to overestimate monomer concentrations.
- Higher aggregates than the dimer can be present, especially at lower temperatures, even where an isosbestic point is observed for monomer-dimer equilibrium. This results in errors in the calculated dimerization constant, K . It is important to prove that K is constant over a range of dye concentrations at a given temperature.
- The ionic strength of the dye solutions at concentrations less than $1 \times 10^{-5} \text{ M}$ are close to zero and the activity coefficients of the dye species are close to unity.

- Absorption of dye to glass surfaces was observed. Absorbance data should be collected on freshly-made solutions.
- In the temperature ranges 25 to 75°C for CoTSPC dimerization in pure water, a positive ΔC_p° was found which indicates that the reaction is not caused by the structure-making property of water molecules surrounding the dye molecule, i.e., hydrophobic bonding.
- We believe that CoTSPC aggregates because the electric charges are dispersed by the solvent (water) molecule and additional Van der Waals forces are also present between the planar hydrophobic groups in the dye molecule.
- In alcohol-water mixtures, when compared at a constant mole fraction of the alcohol, the dimerization constant decreases as the alkyl group changes from MeOH to EtOH and i-PrOH. As this is the trend for increasing water structure in the solution, aggregation of CoTSPC is not favored by the structure-making effect of the water molecules.
- CoTSPC dissolves more readily in MeOH than in EtOH or i-PrOH (and dimerizes faster in MeOH-H₂O than in EtOH-H₂O and i-PrOH-H₂O solutions of the same mole fraction). A shift of the monomer peak to a lower wavelength was found in pure methanol only but the monomer peak remains in the same position in pure water, ethanol, and isopropanol. The above statements indicate that a special solvation of CoTSPC by methanol, due perhaps to its high polarity, may be present; however, this solvation effect does not cause any dimerization of CoTSPC in pure methanol.

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APPENDIX A
ABSORPTION OF DYE TO GLASS WALL AT 35°C

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APPENDIX A

ABSORPTION OF DYE TO GLASS WALL AT 35°C

$C_{T,M}$	Dye*	A (662nm)
7.98×10^{-6}	fresh	0.506
	1 day	0.503
6.85×10^{-6}	fresh	0.456
	7 days	0.449

*Stored at room temperature in a 100 ml volumetric flask in darkness.

APPENDIX B
PHYSICAL PROPERTIES OF SOLVENT SYSTEMS

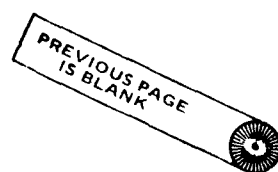


Table D-3. Dielectric Constant of Water

$t, ^\circ\text{C}$	ϵ
5	85.90
15	82.04
25	78.36
35	74.85
45	71.50
55	68.30
65	65.25
75	62.34

Table D-2. 40% EtOH (0.15 x_2) at 25°C

Conc.	Aobs	A1	A2	A3	A4
0.0839	0.102	0.101	0.102	0.100	0.101
0.102	0.121			0.122	0.122
0.136	0.161	0.163	0.165	0.162	0.163
0.272	0.321			0.322	0.322
0.340	0.400	0.401	0.403	0.400	0.401
0.679	0.787	0.783	0.782	0.783	0.783
0.839	0.956	0.959	0.958	0.959	0.958
2.04	2.20	2.20	2.20	2.20	2.20
Corr. $f = 1.00$					
ΣSQ		2.7E-5	3.8E-5	2.9E-5	3.0E-5
$\epsilon_M \times 10^{-5} \pm SD$		1.21 0.02	1.23 f	1.20 0.01	1.21 f
$\epsilon_D \times 10^{-5} \pm SD$		1.03 0.84	1.50 0.10	0.768 0.892	1.07 0.20
$K \times 10^{-5} \pm SD$		0.0707 0.729	0.166 0.031	0.0528 0.0436	0.0737 0.0156

Table D-1. 40% EtOH (0.15 X₂) at 15°C

Conc.	Aobs	A corr.	A1	A2	A3
0.839	0.103	0.102	0.101	0.101	0.101
0.102	0.122	0.121		0.122	0.122
0.136	0.163	0.161	0.163	0.163	0.162
0.272	0.324	0.321		0.321	0.321
0.340	0.401	0.397	0.400	0.400	0.399
0.679	0.791 (0.787)	0.783 (0.779)	0.774	0.773	0.773
0.839	0.946	0.937	0.943	0.941	0.942
2.04	2.10	2.08	2.10	2.08	2.08
Corr. f = 0.99					
ΣSQ			1.4E-4	7.0E-5	7E-5
$\epsilon_M \times 10^{-5} \pm SD$			1.22 0.04	1.21 0.02	1.21 f
$\epsilon_D \times 10^{-5} \pm SD$			0.107 2.70	<0	<0
$K \times 10^{-5} \pm SD$			0.0563 0.103	0.0321 0.0376	0.0297 0.0117

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APPENDIX D

ABSORBANCES AND LEAST-SQUARES FIT FOR ALCOHOL-WATER SOLUTIONS

Table C-8. Data at 75°C

Conc. x 10 ⁵ , M	A obs	A corr	A1	A2	A3	A4	A5	A6	A7	A8	A9
0.00879	0.010	0.0102	0.0102	0.0104	0.0967	0.0105	0.00967	0.00999	0.00971	0.00101	0.0103
0.0188	0.020	0.0204	0.0214	0.0218	0.0205	0.0220	0.0205	0.0207	0.0206	0.0210	0.0215
0.0195	0.021	0.0214	0.0222	0.0226	0.0213	0.0228	0.0213	0.0215	0.0213	0.0218	0.0224
0.0227	0.024	0.0245	0.0257	0.0262	0.0247	0.0264	0.0247	0.0249	0.0247	0.0252	0.0257
0.0252	0.027	0.0275	0.0284	0.0289	0.0274	0.0292	0.0273	0.0275	0.0274	0.0278	0.0284
0.0336	0.036	0.0367	0.0374	0.0380	0.0364	0.0385	0.0362	0.0362	0.0363	0.0365	0.0373
0.0440	0.046	0.0469	0.0484	0.0490	0.0473	0.0498	0.0471	0.0469	0.0471	0.0472	0.0481
0.0523	0.054	0.0551	0.0570	0.0577	0.0559	0.0586	0.0556	0.0553	0.0556	0.0556	0.0565
0.0911	0.093	0.0949	0.0957	0.0964	0.0954	0.0983	0.0947	0.0944	0.0946	0.0941	0.0949
0.114	0.115	0.117	0.118	0.118	0.118	0.121	0.117	0.117	0.117	0.116	0.117
0.209	0.203	0.207	0.205	0.205	0.208	0.209	0.207	-	0.207	0.207	0.205
0.523	0.474	0.483	0.471	0.471	0.476	0.474	0.483				0.483
0.671	0.583	0.595	0.590	0.590	0.593	0.591					
0.681	0.589	0.601	0.598	0.598	0.601	0.599					
0.789	0.663	0.676	0.691	0.691	0.690	0.690					
0.879	0.735	0.750	0.755	0.755	0.751	0.752					
0.977	0.815	0.831	0.831	0.824	0.826						
1.68	1.34	1.37	1.37	1.37							
Corr. f = 1.02											
zsq			4.6 E-4	4.6 E-4	3.2 E-4	3.9 E-4	9.9 E-7	9.0 E-7	9.4 E-7	2.7 E-6	1.1 E-5
$\epsilon_M \times 10^{-5} \pm SD$			1.18 0.09	1.21 f	1.11 0.05	1.21 f	1.11 0.01	1.21 f	1.12 0.01	1.21 f	1.21 f
$\epsilon_D \times 10^{-5} \pm SD$			1.32 0.05	1.33 0.03	0.957 0.260	1.20 0.09	1.35 0.04	1.89 0.03	1.48 0.15	1.77 0.03	1.57 0.02
$K \times 10^{-5} \pm SD$			2.39 1.46	2.94 0.43	0.638 0.450	1.91 0.050	1.25 0.021	30.0 7.3	1.78 0.93	14.4 2.7	5.99 0.81

Table C-7. Data at 65°C

Conc. x 10 ⁵ , M	A obs	A corr.	A1	A2	A3	A4	A5	A6	A7	A8	A9
0.00879	0.010	0.0102	0.0101	0.0104	0.0975	0.0104	0.00973	0.00103	0.00987	0.0102	0.0101
0.0188	0.021	0.0214	0.0213	0.0218	0.0206	0.0219	0.0207	0.0214	0.0208	0.0211	0.0210
0.0195	0.021	0.0214	0.0221	0.0226	0.1014	0.0227	0.0214	0.0222	0.0215	0.0219	0.0217
0.0227	0.024	0.0245	0.0256	0.0261	0.0248	0.0263	0.0248	0.0257	0.0249	0.0253	0.0251
0.0252	0.026	0.0265	0.0283	0.0289	0.0275	0.0291	0.0283	0.0276	0.0276	0.0279	0.0277
0.0336	0.036	0.0367	0.0372	0.0379	0.0364	0.0382	0.0363	0.0372	0.0364	0.0366	0.0364
0.0440	0.046	0.0469	0.0481	0.0489	0.0473	0.0493	0.0470	0.0478	0.0471	0.0471	0.0470
0.0523	0.055	0.0561	0.0566	0.0574	0.0558	0.0580	0.0555	0.0562	0.0555	0.0554	0.0553
0.0911	0.092	0.0933	0.0947	0.0956	0.0945	0.0968	0.0938	0.0939	0.0936	0.0932	0.0934
0.114	0.113	0.115	0.116	0.117	0.117	0.119	0.116	0.115	0.115	0.115	0.115
0.209	0.199	0.203	0.201	0.020	0.203	0.024	0.203	0.201	0.203	0.203	
0.523	0.460	0.469	0.456	0.456	0.460	0.458	0.469	0.469			
0.671	0.562	0.573	0.570	0.569	0.571	0.570					
0.681	0.565	0.576	0.577	0.577	0.579	0.578					
0.789	0.635	0.648	0.665	0.665	0.664	0.664					
0.879	0.713	0.727	0.725	0.725	0.722	0.723					
0.977	0.781	0.797	0.797	0.797	0.792	0.793					
1.58	1.27	1.30	1.30	1.30							
Corr. f = 1.02											
ES?											
$\epsilon_M \times 10^{-5} \pm SD$											
			4.8 E-4	4.9 E-4	4.2 E-4	4.6 E-4	2.9 E-6	9.3 E-6	2.7 E-6	3.7 E-6	3.3 E-6
			1.17 0.08	1.21 f	1.12 0.06	1.21 f	1.13 0.01	1.21 f	1.14 0.03	1.21 f	1.21 f
$\epsilon_D \times 10^{-5} \pm SD$											
			1.18 0.05	1.20 0.03	0.953 0.228	1.12 0.09	1.32 0.05	1.47 0.02	1.43 0.15	1.65 0.04	1.73 0.08
$K \times 10^{-5} \pm SD$											
			2.14 1.16	2.65 0.35	0.911 0.677	2.08 0.55	1.83 0.44	5.29 0.58	3.08 2.05	9.88 1.85	13.6 5.0

Table C-6. Data at 55°C

Conc. $\times 10^5, M$	A obs	A corr.	A1	A2	A3	A4	A5	A6	A7	A8
0.00879	0.010	0.0101	0.00096	0.00981	0.0104	0.00966	0.00940	0.00133	0.00957	0.00100
0.0188	0.020	0.0202	0.0200	0.0207	0.0217	0.0204	0.0199	0.0213	0.0201	0.0205
0.0195	0.021	0.0212	0.0207	0.0214	0.0225	0.0211	0.0206	0.0220	0.0209	0.0213
0.0227	0.024	0.0242	0.0240	0.0248	0.0260	0.0245	0.0240	0.0254	0.0242	0.0246
0.0252	0.025	0.0253	0.0266	0.0274	0.0287	0.0271	0.0265	0.0281	0.2068	0.0272
0.0336	0.035	0.0354	0.0352	0.0362	0.0377	0.0358	0.0351	0.0367	0.0353	0.0356
0.0440	0.045	0.0455	0.0458	0.0467	0.0485	0.0464	0.0456	0.0471	0.0457	0.0458
0.0523	0.054	0.0545	0.0042	0.0550	0.0569	0.0547	0.0539	0.0553	0.0538	0.0538
0.0911	0.091	0.0919		0.0921	0.0942	0.0920	0.0913	0.0917	0.0909	0.0904
0.114	0.110	0.111		0.113	0.115	0.113	0.113	0.112	0.112	0.111
0.209	0.195	0.197		0.194	0.196	0.195	0.196	0.194	0.197	0.197
0.523	0.440	0.444		0.432	0.432	0.433	0.444	0.445		
0.671	0.530	0.535		0.535	0.535	0.536				
0.681	0.533	0.538		0.542	0.542	0.543				
0.798	0.599	0.605		0.621	0.621	0.621				
0.879	0.674	0.681		0.675	0.674	0.674				
0.977	0.735	0.742		0.739	0.739	0.737				
1.68	1.17	1.18		1.18	-	-				
ΣSQ			2.4 E-5	4.9 E-4	5.2 E-4	4.8 E-4	6.2 E-6	2.8 E-5	5.2 E-6	7.1 E-6
$\epsilon_M \times 10^{-5} \pm SD$			1.21 f	1.13 0.07	1.21 f	1.11 0.07	1.08 0.02	1.21 f	1.11 0.04	1.21 f
$\epsilon_D \times 10^{-5} \pm SD$			1.96 0.11	0.919 0.064	0.976 0.093	0.827 0.215	0.906 0.156	1.31 0.04	1.41 0.24	1.63 0.05
$K \times 10^{-5} \pm SD$			120.4 175.4	1.47 0.64	2.33 0.59	1.10 0.79	0.877 0.307	5.50 0.82	2.78 2.67	15.0 3.74

Table C-5. Data at 45°C

Cc	A6	A5	A4	A3	A2	A1	A corr.	Aobs	$\times 10^5, M$
0.00879	0.00999	0.00101	0.00972	0.00938	0.00947	0.00965	0.0101	0.010	0.00879
0.0122	0.0204	0.0209	0.0199	0.0197	0.0199	0.0202	0.0202	0.020	0.0122
0.0135	0.0211	0.0216	0.0206	0.0204	0.0207	0.0210	0.0212	0.020	0.0135
0.0227	0.0243	0.0249	0.0238	0.0237	0.0239	0.0243	0.0222	0.022	0.0227
0.0252	0.0268	0.0274	0.0263	0.0262	0.0265	0.0268	0.0253	0.025	0.0252
0.0336	0.0349	0.0357	0.0344	0.0345	0.0349	0.0353	0.0343	0.034	0.0336
0.0440	0.0447	0.0456	0.0444	0.0445	0.0451	0.0455	0.0448	0.044	0.0440
0.0523	0.0524	0.0533	0.0522	0.0524	0.0530	0.0534	0.0535	0.053	0.0523
0.0911	0.0863	0.0877	0.0881	0.0877	0.0886	0.0886	0.0879	0.087	0.0911
0.114									0.114
0.209	0.185	0.183		0.185	0.185	0.184	0.185	0.183	0.209
0.523	0.415	0.415		0.415	0.404	0.403	0.415	0.411	0.523
0.671					0.498	0.497	0.497	0.492	0.671
0.631					0.504	0.503	0.501	0.496	0.631
0.798					0.575	0.575	0.558	0.552	0.798
0.879					0.623	0.624	0.629	0.623	0.879
0.977					0.680	0.682	0.685	0.678	0.977
1.68					-	1.08	1.08	1.07	1.68
Vol. corr. f = 1.0									
TSQ	9.9 E-6	2.0 E-5	6.0 E-6	5.2 E-6	4.8 E-4	4.9 E-4			
$\epsilon_1 \times 10^{-5} \pm SD$	1.21 f	1.21 f	1.21 f	1.08 0.02	1.09 0.09	1.12 0.08			
$\epsilon_2 \times 10^{-5} \pm SD$	1.40 0.07	1.19 0.04	0.170 0.11	0.976 0.074	0.706 0.197	0.804 0.060			
$K \times 10^{-5} \pm SD$	11.1 2.37	6.18 0.87	32.3 19.8	1.78 0.46	1.28 0.90	1.76 0.80			

Table C-4. Data at 35°C

Conc. x 10 ⁵ , M	Abs	A1	A2	A3	A4	A5	A6	A7
0.00879	0.010		0.0091	0.00911	0.0090	0.0098	0.00926	0.00955
0.0188	0.020		0.0191	0.0191	0.0190	0.0197	0.0190	0.0193
0.0195	0.021		0.0198	0.0197	0.0197	0.0204	0.0197	0.0200
0.0227	0.021		0.0230	0.0228	0.0228	0.0234	0.0227	0.0230
0.0252	0.024	0.024	0.0253	0.0252	0.0251	0.0258	0.0251	0.0253
0.0336	0.033		0.0333	0.0331	0.0331	0.0334	0.0329	0.0329
0.0440	0.042		0.0429	0.0426	0.0426	0.0426	0.0426	0.0422
0.0523	0.051		0.0504	0.0500	0.0500	0.0497	0.0503	0.0494
0.0911	0.082	0.084	0.0837	0.0828	0.0830	0.0817		0.0824
0.114								
0.209	0.172	0.170	0.173	0.172	0.172	0.172		
0.523	0.379	0.365	0.369	0.379				
0.671	0.451	0.449	0.452					
0.681	0.456	0.454	0.457					
0.789	0.506	0.519	0.519					
0.879								
0.977	0.613	0.625	0.611					
1.68	0.975	0.971						
Vol. corr. f = 1.00								
ΣSQ		4.5 E-4	3.3 E-4	9.6 E-6	9.5 E-6	1.4 E-5	8.3 E-6	1.0 E-5
$\epsilon_M \times 10^{-5} \pm SD$	1.17 0.23	1.05 0.07	1.05 0.07	1.06 0.03	1.05 0.04	1.21 f	1.21 f	1.21 f
$\epsilon_D \times 10^{-5} \pm SD$	0.756 0.075	0.542 0.163	0.542 0.163	0.846 0.084	0.653 0.728	1.26 0.07	1.72 0.23	1.46 0.15
$K \times 10^{-5} \pm SD$	3.46 3.24	1.36 0.77	1.36 0.77	2.25 0.72	1.57 1.87	1.40 3.4	83.6 138.1	26.4 15.6

Table C-3. Data at 25°C

Conc. x 10 ⁵ , M	Aobs	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
0.00879	0.0095		0.0089	0.0091	0.0088	0.0098	0.0088	0.0089	0.0093	0.0095	0.0093
0.0188	0.018		0.0185	0.0184	0.0183	0.0197	0.0184	0.0184	0.0186	0.0191	0.0186
0.0195	0.020		0.0191	0.0190	0.0190	0.0203	0.0190	0.0191	0.0193	0.0197	0.0192
0.0227	0.021		0.0221	0.0219	0.0219	0.0233	0.0220	0.0220	0.0221	0.0226	0.0221
0.0252	0.024	0.024	0.0244	0.0241	0.0242	0.0256	0.0242	0.0242	0.0242	0.0247	0.0243
0.0336	0.032		0.0320	0.0315	0.0317	0.0330	0.0317	0.0316	0.0316	0.0319	0.0315
0.0440	0.040		0.0410	0.0406	0.0406	0.0417	0.0406	0.0405	0.0403	0.0405	0.0403
0.0523	0.048		0.0480	0.0477	0.0475	0.0484	0.0475	0.0474	0.0472	0.0472	0.471
0.0911	0.078	0.079	0.0788		0.0781	0.0778	0.0780	0.0781	0.0782	0.0768	0.0783
0.114											
0.209	0.160	0.157	0.160		0.160	0.158	0.160			0.160	
0.523	0.346	0.333	0.338		0.346	0.347					
0.671	0.411	0.410	0.412								
0.631	0.420	0.415	0.417								
0.798	0.457	0.474	0.474								
0.879											
0.977	0.566	0.571	0.557								
1.68	0.894	0.890									
Vol. corr. f = 1.00											
ΣQ	5.3 E-4	4.4 E-4	4.4 E-4	2.7 E-6	3.2 E-6	2.1 E-5	3.2 E-6	3.2 E-6	3.8 E-6	6.5 E-6	3.4 E-6
$\epsilon_M \times 10^{-5} \pm SD$	1.19 0.36	1.03 0.10	1.03 0.10	1.21 f	1.03 0.02	1.21 f	1.04 0.03	1.06 0.09	1.19 0.33	1.21 f	1.21 f
$\epsilon_D \times 10^{-5} \pm SD$	0.723 0.070	0.539 0.152	0.539 0.152	1.54 0.14	0.714 0.044	0.916 0.031	0.760 0.227	1.06 0.06	1.34 0.26	1.13 0.04	1.37 0.08
$K \times 10^{-5} \pm SD$	5.84 7.36	2.00 1.37	2.00 1.37	62.4 44.8	2.55 0.44	9.37 1.11	2.84 1.62	5.57 10.2	27.5 74.4	16.8 2.6	32.8 10.4

Table C-2. Data at 15°C

Conc. $\times 10^5, M$	A6bs	A1	A2	A3	A4	A5	A6
0.00879	0.0095		0.00814	0.00713	0.00825	0.00941	0.00840
0.0188	0.017		0.0170	0.0153	0.0171	0.0185	0.0170
0.0195	0.018		0.0176	0.0158	0.0177	0.0191	0.0176
0.0227	0.019	0.022	0.0203	0.0184	0.0204	0.0219	0.0203
0.0252	0.022		0.0225	0.0203	0.0225	0.0239	0.0223
0.0336	0.029		0.0294	0.0270	0.0294	0.0306	0.0293
0.0440	0.038		0.0378	0.0352	0.0376	0.0385	0.0377
0.0523	0.045		0.0442	0.0416	0.0439	0.0446	0.0445
0.0911	0.072	0.073	0.0723	0.0708	0.0718	0.0712	
0.114							
0.209	0.146	0.144	0.147	0.152	0.146	0.144	
0.523	0.317	0.307	0.311	0.319	0.317	0.318	
0.671	0.375	0.377	0.380	0.379			
0.631	0.395	0.382	0.384	0.383			
0.798	0.419	0.436	0.436	0.423			
0.879							
0.977	0.520	0.525	0.513				
1.68	0.824	0.820					
Vol. Corr. $f = 1.00$							
ΣS_Q	6.4 E-4	5.3 E-4	2.5 E-4	4.1 E-6	2.4 E-5	5.6 E-6	
$\epsilon_M \times 10^{-5} \pm SD$	1.10 0.39	0.949 0.110	0.821 0.038	1.21 f	1.21 f	1.21 f	
$\epsilon_D \times 10^{-5} \pm SD$	0.669 0.077	0.484 0.169	<0	0.690 0.043	0.872 0.023	1.50 0.16	
$K \times 10^{-5} \pm SD$	5.92 8.92	1.92 1.54	0.136 0.146	3.20 0.68	15.2 1.9	158.5 188.3	

Table C-1. Data at 5°C

Conc. $\times 10^5, M$	Aobs	A1	A2	A3	A4	A5	A6	A7	A8
0.00879	0.0093	0.00843	0.0083			0.0084	0.00766	0.00781	0.00885
0.0188	0.016	0.0162	0.0163			0.0168	0.0159	0.0160	0.0171
0.0195	0.017	0.0167	0.0168			0.0173	0.0164	0.0165	0.0177
0.0227	0.018	0.0191	0.0192	0.0174	0.018	0.0199	0.0190	0.0190	0.0201
0.0252	0.021	0.0208	0.0211			0.0218	0.0209	0.0209	0.0219
0.0336	0.027	0.0266	0.0272			0.0280	0.0273	0.0272	0.0280
0.0440	0.034		0.0346			0.0354	0.0349	0.0346	0.0351
0.0523	0.041		0.0403	0.0406	0.041	0.0410	0.0408	0.0403	0.0406
0.0911	0.065			0.0652	0.066	0.0654	0.0664	0.0655	0.0648
0.114									
0.209	0.134			0.134	0.135	0.130	0.134	0.134	0.132
0.523	0.294			0.294	0.285	0.281	0.284	0.294	0.295
0.671	0.344				0.347	0.347	0.348		
0.681									
0.789	0.388			0.398		0.402	0.400		
0.979									
0.977	0.480				0.474	0.479	0.472		
1.68	0.770					0.767			
Vol. corr. $f = 1.00$									
ϵ_{SQ}		2.2 E-6	4.7 E-6	8.9 E-7	2.3 E-4	4.1 E-4	3.4 E-4	4.6 E-6	1.5 E-5
$\epsilon_1 \times 10^{-5} \pm SD$		1.21 f	1.21 f	0.824 0.027	0.834 0.139	1.03 0.20	0.899 0.114	0.935 0.032	1.21 f
$\epsilon_2 \times 10^{-5} \pm SD$		0.938 0.441	1.15 0.18	0.619 0.076	0.379 0.252	0.672 0.038	1.518 0.127	0.746 0.034	0.859 0.019
$K \times 10^{-5} \pm SD$		44.0 41.5	69.3 46.1	2.02 0.75	1.41 1.69	8.03 6.66	2.70 2.24	5.59 1.54	27.0 2.96

APPENDIX C
ABSORBANCES AND LEAST-SQUARES FIT FOR WATER SOLUTIONS

PREVIOUS PAGE
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Table B-1. Correction Factors for Solvent Expansion

Temp °C	Density of pure water, g/ml	Correction factor, f, for absorbances*
5	1.00	1.00
15	0.999	1.00
25	0.997	1.00
35	0.994	1.00
45	0.990	1.01
55	0.986	1.01
65	0.981	1.02
75	0.975	1.02

*A corr = Aobs x f

Table B-2. Some Properties of ROH-H₂O Mixture at 25°C*

Solvent mixture	X ₂ , mole fraction	Viscosity, c _p	Dielectric constant
H ₂ O	0	0.89	78.5
MeOH	0.10	1.24	71.5
EtOH	0.10	1.90	65.5
i-PrOH	0.10	2.15	59.7

*From Reference 15



Table D-4. 40% EtOH (0.15 X_2) at 35°C

Conc.	Aobs	A1	A2	A3
0.0839	0.102	0.0998	0.101	0.101
0.102	0.120	0.121	0.122	0.122
0.136	0.160	0.161	0.163	0.162
0.272	0.320	0.320	0.322	0.321
0.340	0.397	0.398	0.400	0.399
0.679	0.785	0.781	0.781	0.780
0.839	0.954	0.957	0.956	0.956
2.04	2.10 (2.20)	2.20	2.20	
Corr. f				
ΣSQ		3.5E-5	4.6E-5	4.5E-5
$\epsilon_M \times 10^{-5} \pm SD$		1.20 0.01	1.21 f	1.21 f
$\epsilon_D \times 10^{-5} \pm SD$		0.417 1.73	1.32 0.16	1.73 0.56
$K \times 10^{-5} \pm SD$		0.0375 0.0453	0.101 0.023	0.189 0.222

Table D-5 40% EtOH (0.15 X_2) at 45°C

Conc.	Aobs	A corr	A1	A2	A3	A4
0.0839	0.101	0.102	0.101	0.00995	0.00992	0.100
0.102	0.119	0.120	0.122	0.121	0.121	0.122
0.136	0.158	0.160	0.163	0.161	0.161	0.162
0.272	0.317	0.320	0.323	0.320	0.320	0.320
0.340	0.394	0.398	0.402	0.398	0.399	0.398
0.679	0.780	0.786	0.785	0.785	0.786	0.784
0.839	0.952	0.962	0.961 0.220	0.963 2.20	0.962	0.963
2.04	2.11	2.13				
Corr. f = 1.01						
ΣSQ			3.9E-5	1.1E-5	9.4E-6	1.7E-5
$\epsilon_M \times 10^{-5} \pm SD$			1.21 f	1.19 0.01	1.18 0.01	1.21 f
$\epsilon_D \times 10^{-5} \pm SD$			0.728 0.361	5.5 3.7	2.69 0.40	2.09 0.09
$\kappa \times 10^{-5} \pm SD$			0.0534 0.0154	<0	<0	0.580 0.347

Table D-6. 40% EtOH (0.15 X₂) at 55°C

Conc.	Aobs	A corr.	A1	A2	A3
0.0839	0.100	0.102	0.101	0.100	0.00994
0.102	0.118	0.120	0.123	0.122	0.121
0.136	0.156	0.159	0.163	0.162	0.161
0.272	0.315	0.321	0.324	0.320	0.320
0.340	0.390	0.398	0.403	0.398	0.399
0.679	0.771	0.786	0.787	0.785	0.786
0.839	0.946	0.965	0.962	0.966	0.966
2.04	2.10	2.14	2.14		
Corr. f = 1.02					
ΣSQ			6.5E-5	1.58E-5	1.3E-5
$\epsilon_M \times 10^{-5} \pm SD$			1.21 f	1.21 f	1.19 0.01
$\epsilon_D \times 10^{-5} \pm SD$			9.92 7.38	2.15 0.07	<0
$K \times 10^{-5} \pm SD$			<0	0.822 0.481	0.0106 0.255

Table D-7. EtOH - Water, 20% EtOH

$X_2 = 0.08$	Temp. ϵ	25			35		45		
C_T	Vol. f	$\frac{1}{\Lambda \text{ corr}}$	Λf	Λf	$\frac{1}{\Lambda \text{ corr}}$	f	$\frac{1.01}{\Lambda \text{ corr}}$	Λf	Λf
4.66E-6		0.440	0.447	0.444	0.437		0.454	0.455	0.458
8.92E-6		0.791	0.807	0.816	0.806		0.834	0.839	0.839
9.32E-6		0.844	0.840	0.851	0.861		0.879	0.874	0.874
1.17E-6		1.05	1.03	1.05	1.07		1.09	1.08	1.08
1.56E-5		1.32	1.32	1.39	1.35		1.39	1.42	1.42
1.63E-5		1.43	1.40	1.44	1.47		1.50	1.48	1.48
2.33E-5		1.92 (1.96)	1.95	2.03	2.03		2.07	2.07	2.07
Σ_{SQ}			2.2 E-3	2.4 E-3		2.2 E-3		1.39 E-3	1.41 E-3
$\Sigma_M \times 10^{-5} \pm SD$			1.21 f	1.21 f		1.00 0.29		1.08 0.34	1.21 f
$\Sigma_D \times 10^{-5} \pm SD$			1.37 0.10	1.57 0.09		1.46 0.66		1.50 0.39	1.56 0.07
$K \times 10^{-5} \pm SD$			1.87 0.90	4.23 3.25		0.402 0.264		6.82 3.33	2.57 1.31

APPENDIX E
BLANDAMER'S METHOD FOR CALCULATING ΔH and ΔC_p

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APPENDIX E BLANDAMER'S METHOD FOR CALCULATING ΔH and ΔC_p

Blandamer's expression for computing thermodynamic parameters from the temperature dependence of rate data is

$$K = \frac{k_0 T}{T_0} \cdot \exp \left\{ \frac{\Delta H_0^\ddagger}{R} \left[\frac{1}{T_0} - \frac{1}{T} \right] + \frac{\Delta C_p^\ddagger}{R} \left[\ln \left(\frac{1}{T_0} \right) + \frac{T_0}{T} - 1 \right] \right\} \quad (E-1)$$

where k = rate coefficient at temperature, T

T = temperature

k_0 = rate coefficient at temperature, T_0

ΔH_0^\ddagger = enthalpy of activation at T_0

ΔC_p^\ddagger = heat capacity of activation

Equation (E-1) is obtained by integrating the vant-Hoff isochore between temperatures T_0 and T assuming ΔC_p^\ddagger is independent of temperature. For a given set of k , T data pairs, one pair of K and T are set as K_0 and T_0 , and the remaining values of K , T are used in a regression of Equation (E-1) to find a value of ΔH^\ddagger and ΔC_p^\ddagger at T_0 . Another pair of k , T are set as the new K_0 , T_0 and values of ΔH^\ddagger and ΔC_p^\ddagger at the new T_0 are obtained. The process is repeated until each value of K , T in the data set has been assigned K_0 , T_0 yielding values of ΔH^\ddagger and ΔC_p^\ddagger for each temperature, T . Any data set produces:

- (a) ΔC_p^\ddagger zero, ΔH^\ddagger constant with temperature;
- (b) ΔC_p^\ddagger constant, ΔH^\ddagger linearly dependent with temperature, or
- (c) ΔC_p^\ddagger temperature dependent.

Equation (E-1) was derived with the assumption that ΔC_p^\ddagger is temperature independent, so for conditions (a) or (b) above, the values of ΔC_p are thermodynamically correct. However, Equation (E-1) gives the correct sign for temperature dependent ΔC_p^\ddagger although the values so computed are not correct since the wrong equation is used to compute ΔC_p^\ddagger . In order to find the values of ΔH^\ddagger and ΔC_p^\ddagger , Equation (E-1) is fit directly with a non-linear, least-squares program¹³ as opposed to the linear form of Equation (E-1) offered by Blandamer.²⁰ To further distinguish between conditions (a) and (b) above, the enthalpies of activation so computed are fit versus temperature with a linear, least-squares version of the program to see if the slope differs from zero.

Table E-1. Calculation of ΔH° and ΔC_p° with Blandamer's Method

T, °C	K, M ⁻¹ x 10 ⁻⁶ (b)	K fit	K fit	K fit	K fit	K fit
25	8.37 ± 0.61(a) (8)	-	8.32	8.32	8.27	8.31
35	4.14 ± 0.48 (8)	4.15	-	4.14	4.14	4.15
45	2.28 ± 0.22 (9)	2.28	2.28	-	2.29	2.27
55	1.38 ± 0.05 (11)	1.37	1.37	1.37	-	1.35
65	0.870 ± 0.003 (11)	0.894	0.894	0.894	0.909	-
75	0.641 ± 0.002 (11)	0.627	0.627	0.626	0.631	0.598
ΔH° , cal/mole		-13,358	-12,187	-11,076	-9,943	-7,413
std dev of mean		135	175	675	138	286
ΔC_p° , cal/mole K		112	111	110	107	98.5
std dev of mean		8	13	9	14	19

aSample standard deviation

bNumber of values of K over the concentration range considered

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